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# A Study of the Physical Properties of Bromopicrin and a Preliminary Investigation of its Reaction in Liquid Ammonia

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A STUDY OF THE PHYSICAL PROPERTIES  
OF BROMOPICRIN AND A PRELIMINARY INVESTIGATION  
OF ITS REACTION IN LIQUID AMMONIA

A STUDY OF THE PHYSICAL PROPERTIES  
OF BROMOPICRIN AND A PRELIMINARY INVESTIGATION  
OF ITS REACTION IN LIQUID AMMONIA

A thesis presented to the Department of Chemistry  
of Union College, in partial fulfillment of the requirements  
for the degree of Bachelor of Science in Chemistry.

By B. Bailey Stone

Approved by

Frederic C. Schmidt

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The author wishes to acknowledge his  
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during the course of this work and for his valuable  
criticisms of this manuscript.

Signed B. Bailey Stone

## INTRODUCTION

It is generally considered that the most important problem of synthetic organic chemistry is to prepare and isolate in the purest possible state compounds which contain new combinations of the carbon atoms with each other and with the atoms of other elements and to pursue a thorough study of their physical and chemical properties. Such compounds serve a greater interest, the more simple their molecular construction. Therefore, such investigations as a rule cannot be undertaken with naturally-occurring compounds, because these are the most complex in structure of all chemical substances. Furthermore, only in a few very rare cases are these compounds subject to direct utilizable results for the technical preparation of other organic compounds. Such investigations are only suitable in the case of substances of a simple structure, since they provide a new insight into the possibilities of reaction of organic compounds and from these reactions may be learned new realizations, which can then be applied to other more complex problems of organic chemistry.

Bromopicrin, mononitrotribromomethane, or nitro-bromoform as it is sometimes called, is just such a simple chemical compound. It is derived from methane, the most simple organic compound that exists, in that it is nothing more than a methane molecule in which the four hydrogen atoms have merely been substituted by three atoms of bromine and a nitro group. It derives the name of bromopicrin from the fact that it is almost the sole product which results when bromine acts destructively on the benzene ring of picric acid.

Bromopicrin is a lemon-yellow colored oily liquid which possesses an indescribably suffocating and extremely penetrating odor. Upon inhalation

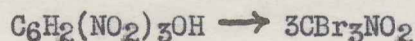


it produces an edema and if the cause of death, the liquid is found to amount to about 58% the total weight of the lungs. Bromopicrin possesses one-eighth the lethal activity of chloropicrin which was used in poisonous gas shells during the first World War.

#### THE PREPARATION OF BROMOPICRIN

Bromopicrin was first prepared by Stenhouse<sup>1</sup> by the distillation of an aqueous mixture of picric acid, lime and bromine.

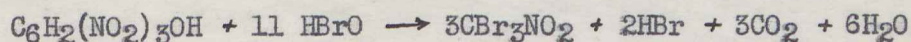
This method was repeated by Bolas and Groves<sup>2</sup>, who claim the conversion of picric acid into bromopicrin is almost quantitative according to the equation



However, according to the work of Scholl and Brenneisen<sup>3</sup> the product does contain minute quantities of dinitro-dibromomethane and carbon tetrabromide.

The exposure of an aqueous solution of picric acid and bromine to direct sunlight for several months produces a yellow oil which is found to be impure bromopicrin<sup>4</sup>. By working in the presence of sodium carbonate, the time of exposure may be reduced to a few days and the yield is practically pure bromopicrin. In the absence of light the reaction requires a longer period for completion.

The reaction according to Orton and McKie<sup>5</sup>, whose experimental measurements of the amount of bromine necessary to decompose a known weight of picric acid and whose estimations of the amount of bromide and bromate formed during the reaction were in close agreement with the equation, is





The best condition for the reaction is a faintly alkaline solution. When prepared in a strongly alkaline or acid solution the yield is poor, since most of the picric acid remains unchanged. The major impurity in all the methods of preparation is carbon tetrabromide, which is present to the extent of about .5% by weight.

The bulk of the bromopicrin used during the course of this work was prepared according to the method of Bolas and Groves<sup>2</sup>, which is also described in a later edition of the *Berichte*<sup>6</sup>. This method is as follows:

10 g. of picric acid is dissolved in 100 cc. of water and heated on a water bath for about an hour with 1.3 g. of calcium oxide to form the calcium salt of picric acid. In about thirty minutes the picric acid will all dissolve and all but a few grains of the calcium oxide. The solution becomes an orange-yellow color. On cooling a light flocculent suspension of the calcium picrate is formed.

A second solution containing 60 g. of calcium oxide in 300 cc. of water is heated to dissolve the oxide, cooled and repeatedly shaken. Then 25 cc. of pure C. P. bromine (77 g.) are added in 2 cc. portions with cooling and shaking to form the calcium hypiodate.

When these two solutions are mixed the bright yellow color of bromopicrin is immediately observed. The solution is steam distilled directly until the yellow color of the bromopicrin disappears and the solution becomes decolorized. The distillate forms two distinct layers, the lower layer containing nearly pure bromopicrin.

The distillate is separated in a separatory funnel and the impure bromopicrin dried with calcium chloride. The dried impure bromopicrin is vacuum distilled and the fraction collected when a constant distillation temperature is



reached. The fraction collected distilled at a temperature range of 69-71° C. at 18-19 mm.

Theoretical yield, 18.99 g. The actual yields using this method varied from about 74% to 78%.

A second method, essentially the same as that of Bolas and Groves<sup>2</sup> proved expedient. The only exception was that the final mixture was distilled directly instead of the usual steam distillation. Here again the distillate formed two immiscible layers, which were separated in the usual manner, the impure bromopicrin dried and vacuum distilled. The actual yields in this case averaged about 83% of the theoretical yield.

An attempt to double the proportions of the reagents in the method of Bolas and Groves<sup>2</sup> gave actual yields of lower values (75%) than before.

A small quantity of bromopicrin was prepared according to the method of Hunter<sup>4</sup>. 10 g. of picric acid in 100 cc. of a 2% solution of sodium carbonate was mixed with 25 cc. (77 g.) of pure bromine and placed in a large flask and set in the light of the sun. After two days standing the yellow oil of bromopicrin began to form. At the end of a five day period the impure bromopicrin was separated from the water-bromine-alkaline solution, dried and vacuum distilled. The bromopicrin distilled at 80° C. at 19 mm. The actual yield was about 60% of the theoretical.

#### THE DETERMINATION OF THE DENSITY

The density was used in conjunction with the boiling point as the criterion of purity during the course of this work and all the bromopicrin prepared was vacuum distilled until a constant value for the density was obtained, which was agreeable with those values previously and most carefully determined.



The procedure followed was that recommended by Findlay<sup>7</sup> and the density was determined at 20° C. A 10 cc. pyknometer proved the most satisfactory.

Data: (Typical)

Weight of Pyknometers Empty

#18	9.0186 g.
#22	8.6819 g.

Determination of Volume with Water at 20°

<u>Time</u>	<u>Weight</u>
3:30	19.0100 g.
6:50	19.0090 g.
10:40	19.0080 g.
0:00	19.0110 g.
4:50	18.6634 g.
6:25	18.6630 g.
10:05	18.6620 g.
0:00	18.6646 g.

Weight filled with Bromopicrin at 20°

<u>Time</u>	<u>Weight</u>
2:14:30	36.9816 g.
2:20:00	36.9810 g.
2:22:00	36.9808 g.
2:24:00	36.9806 g.
2:26:00	36.9804 g.
2:28:00	36.9802 g.
2:46:00	36.6239 g.
2:56:30	36.6233 g.
2:59:00	36.6230 g.
3:01:00	36.6228 g.
3:03:00	36.6226 g.
3:05:00	36.6224 g.

Calculation of Volumes

#18	$\frac{19.0110 - 9.0186}{.9982} = 10.0100 \text{ cc.}$
#22	$\frac{18.6646 - 8.6819}{.9982} = 10.0010 \text{ cc.}$

Calculation of Density of Bromopicrin at 20°

$$\#18 \quad \frac{36.9816 - 9.0186}{10.010} = 2.7935 \text{ g./cc.}$$

$$\#22 \quad \frac{36.6239 - 8.6819}{10.001} = 2.7940 \text{ g./cc.}$$

These values of the density at 20° C. agree very well with those values determined previously by other unknown investigators and as recorded by Beilstein<sup>8</sup> and The Handbook of Chemistry and Physics<sup>9</sup>, which are 2.810 g./cc. at 12° C. and 2.799 g./cc. at 18° C. respectively.

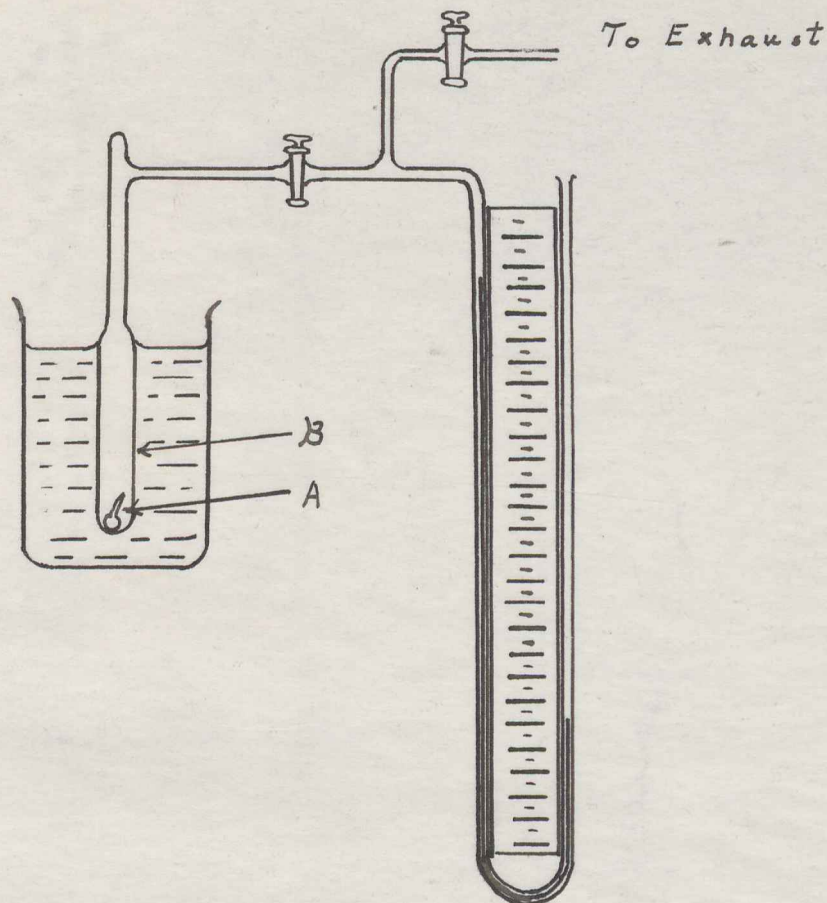
THE DETERMINATION OF THE VAPOR PRESSURE

A great deal of difficulty was experienced in attempting to obtain a vapor pressure curve of bromopicrin. The method of Smith and Menzies<sup>10</sup> was first attempted but was found to be inapplicable in this case since a suitable liquid for the thermostatic bath was not available which would yield high temperatures and still not affect the bromopicrin.

The vapor pressure was then measured with an isotensiscopes according to the method of Smith and Menzies<sup>11</sup> but this method too proved unreliable since the bromopicrin decomposed with the evolution of bromine before a suitable number of readings could be made.

A vapor pressure curve for the bromopicrin was finally obtained in the following manner using the apparatus diagramed below.





The bromopicrin, amounting to approximately 2 grams, was sealed into a small glass bulb A of about 1 cm. radius. The bulb was then placed in the long glass tube B and the glass bulb A broken by shaking the tube. The bromopicrin was then quickly frozen to a white crystalline mass by immersing the tube B in a Dewar flask containing liquid ammonia. While the bromopicrin remained frozen the whole system was evacuated to 3 microns of pressure. The tube B was then placed in a thermostatic bath containing a mixture of glycerol and water and the vapor pressure of the bromopicrin determined at various temperatures until it decomposed. The following data was obtained:

Vap. Press. in mm.	Temp. °C.	Log Vap. Press. in mm.	Reciprocal Abs. Temp.
4.8	18.2 ✓	<del>.6812</del> <sup>.730</sup>	<del>34.3 x 10<sup>-4</sup></del>
5.6	20.1	.7481 ✓	34.1
6.3	23.4 ✓	.7993 ✓	33.7
7.3	30.2	.8633 ✓	33.0
8.6	37.8 ✓	.9345 ✓	32.2
9.4	41.45	.9731 ✓	31.8
9.8	45.5 ✓	.9912 ✓	31.4
11.5	51.1	1.0607 ✓	30.8
<del>12.1</del>	<del>54.6</del> <sup>50</sup>	1.0827 ✓	30.5
<del>13.6</del>	60.8	1.1335 ✓	30.0
14.3	64.5 ✓	1.1553 ✓	29.6
16.6	70.0	1.2201 ✓	29.1
17.5	77.1 ✓	1.245 ✓	28.5
19.0	84.0 ✓	1.280 ✓	28.0
21.7	92.0 ✓	1.338 ✓	27.4
24.5	99.9 ✓	1.390 ✓	26.8
28.1	113.0 ✓	1.450 ✓	25.9
33.8	124.9 ✓	1.530 ✓	25.1
39.8	138.1	1.600	24.3
		1.720	21.0

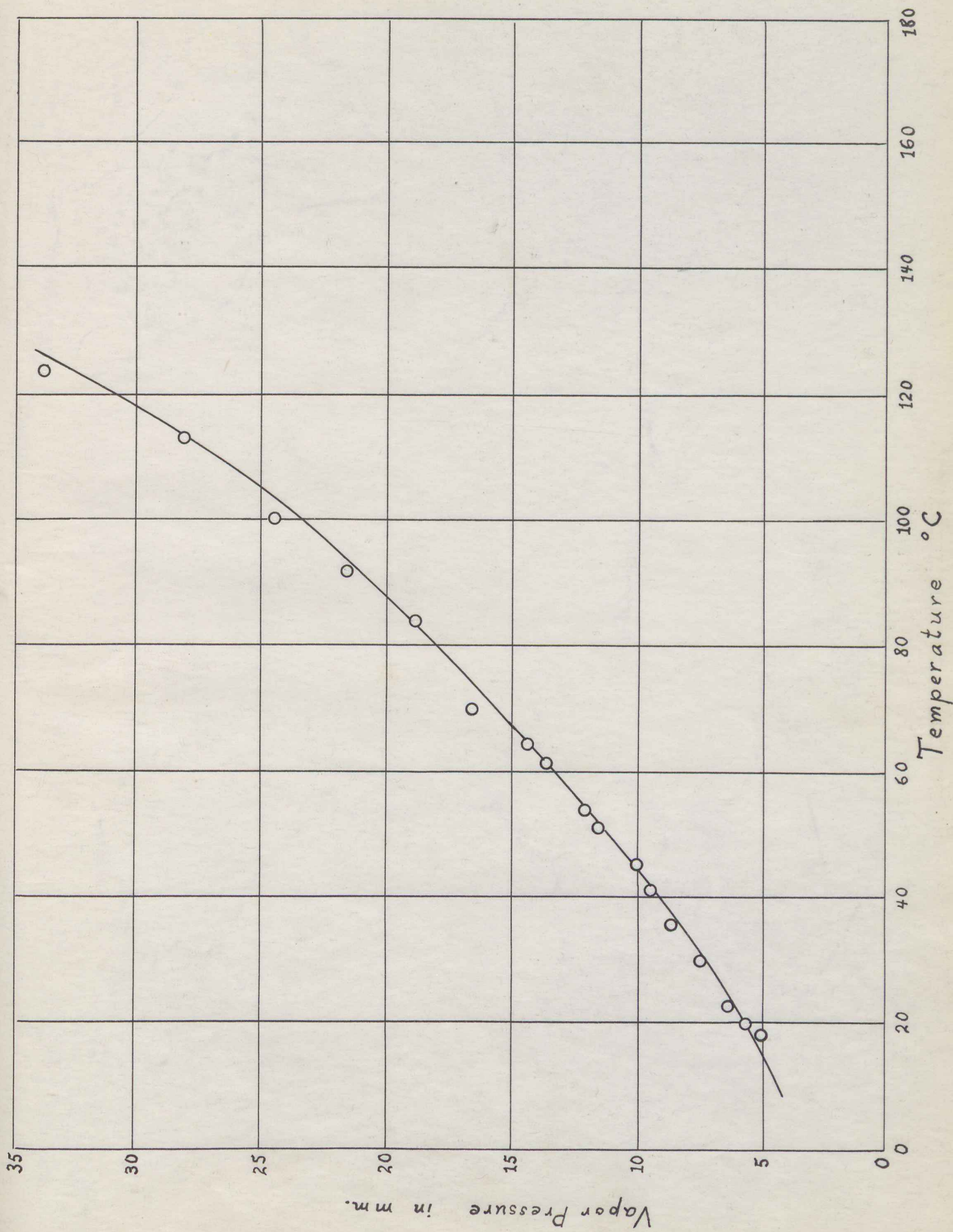
The values above 77.1° C. are not experimentally determined values but are extrapolated values derived from the straight line graph of the log vapor pressure plotted against the reciprocal absolute temperature.

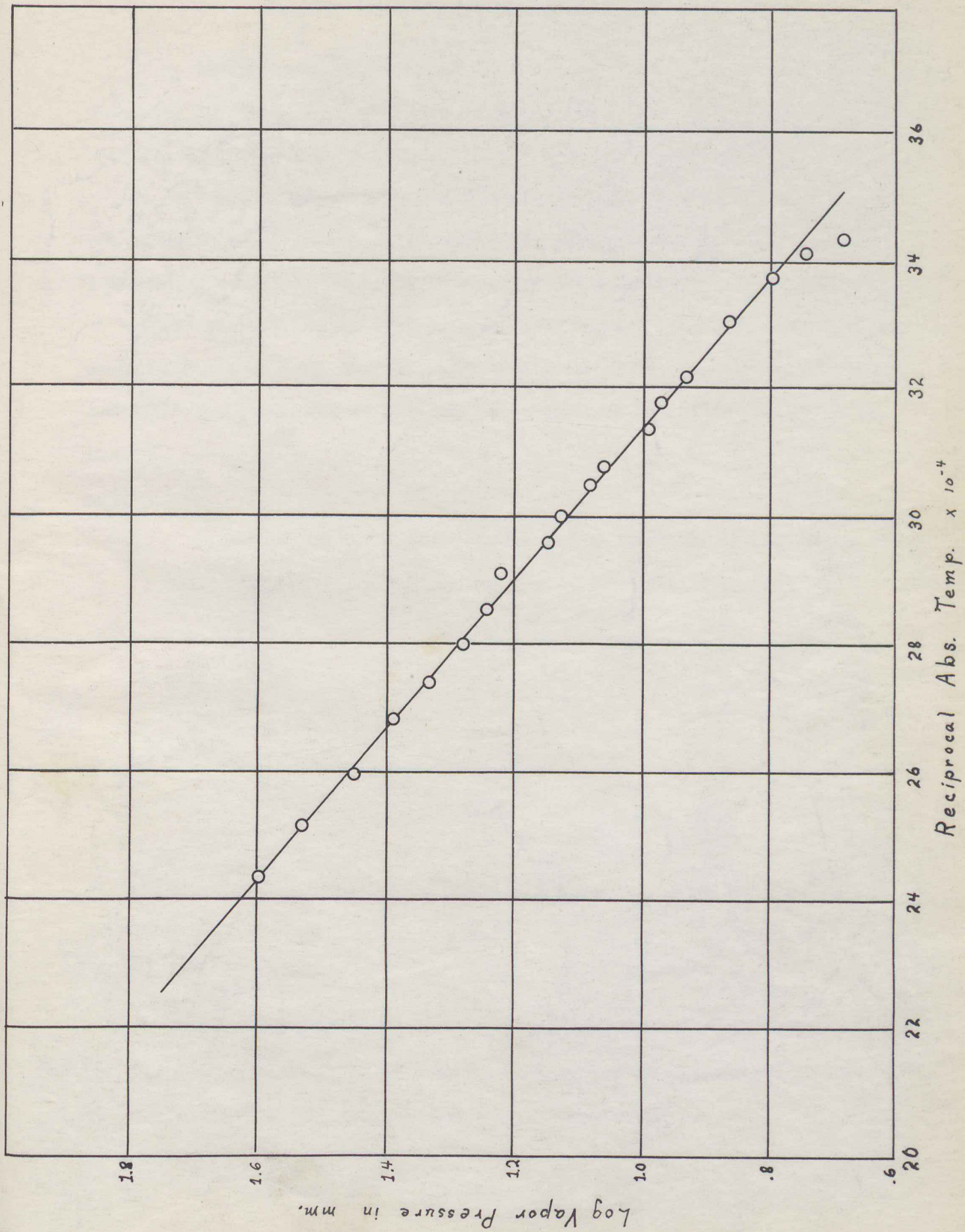
These values are in agreement with the previous values of the literature at low temperatures, but do not agree with those given by Beilstein<sup>8</sup> and the Handbook of Chemistry and Physics<sup>9</sup> at higher temperatures. These two sources state a value of 127° C. at 118 mm. The value as determined by the curve is 127° C. at 34.8 mm. (extrapolated value).

#### THE HEAT OF VAPORIZATION

The heat of vaporization was calculated from the observed values of the pressure and temperature at 20° C. using the Clapeyron equation. This amounted to approximately 20 cal./g. This value is astonishingly low, but it must be considered that the temperature is at 20° C.









## THE DETERMINATION OF THE MELTING POINT

Several determinations of the melting point of pure bromopicrin were made, all of which gave very close checks but which were not in agreement at all with the tabulated value.

The pure bromopicrin was placed in a large test tube with a stirrer and thermometer previously calibrated. The test tube was immersed in a salt solution of water and ice and frozen. The test tube was then placed in a beaker of air and allowed to warm with constant stirring and recording the temperature every half minute. The average value of all the trials for the melting point was  $4.65^{\circ}\text{C.}$ , which differs with the value given by Beilstein<sup>8</sup> of  $10^{\circ}\text{C.}$  by  $5.45^{\circ}\text{C.}$

### Data:

Values of the temperature are given for intervals of one-half a minute.

<u>#I Temp.°C.</u>	<u>#II Temp.°C.</u>	<u>#III Temp.°C.</u>
6.0	-1.0	0.0
5.0	-1.0	1.0
4.8*	- .5	4.0
4.8*	4.0	4.6*
5.1*	4.5*	4.6*
5.1*	4.5*	4.6*
6.0	4.5*	4.8*
6.5	4.6*	5.2
7.0	5.0	5.6
7.0	5.3	6.0
7.5	6.5	6.5
8.0	7.0	7.0
9.0	7.0	7.45
9.5	7.2	7.95
	8.0	8.55
	8.5	9.2
	9.5	

\* Mush

The melting point was also determined using the micro-melting point procedure. The value found with this method proved to coincide very closely with the value determined by the above mentioned method and was  $5.00^{\circ}\text{C.}$

## THE DETERMINATION OF MOLECULAR WEIGHT

During the course of this work in order to be more certain of the purity of the bromopicrin being used, the molecular weight was determined by the cryoscopic method using the Beckmann apparatus, according to the procedure described by Findlay<sup>7</sup>. The solvent was pure anhydrous benzene.

### Typical Data:

Weight of Bulb Empty	6.3662 g.
Weight of Bulb Full	2.6166 g.
Weight of Stem	5.8949 g.
Weight of Bromopicrin	2.1453 g.

Two solutions of different concentration were measured for their freezing point depression:

#1	2.1453 g. $\text{CBr}_3\text{NO}_2$ / 50 cc. $\text{C}_6\text{H}_6$
#2	2.1453 g. $\text{CBr}_3\text{NO}_2$ / 100 cc. $\text{C}_6\text{H}_6$

The density of benzene at 20° C. is .8790 g./cc.

The freezing point constant for benzene is given as 5120.

<u>Concentration</u>	<u>Temperature °C.</u>				<u>Average</u>
0	.8575	.8570	.8568	.8569	.8569
#1	1.7318	1.7320	1.7316	1.7317	1.7317
#2	1.2938	1.2937	1.2940	1.2939	1.2938

This gives the following values for the freezing point depression of the two concentrations:

$$d \text{ (#1)} = .8748^\circ \text{ C.}$$

$$d \text{ (#2)} = .4369^\circ \text{ C.}$$

### Calculation:

The molecular weight was calculated from the formula based upon the integrated Clausius-Clapeyron equation

$$m_1 = kw_1 / dw_2$$



where  $m_1$  is the molecular weight of the solute of mass  $w_1$ ,  $k$  is the freezing point constant for the solvent,  $w_2$  is the weight of solvent and  $d$  is the freezing point depression of the solvent by the solute in degrees.

Concentration #1

$$m_1 = 5120 \cdot 2.1453 / .8748 \cdot 43.95$$

$$d = .8748^\circ \text{C.}$$

$$w_1 = 2.1453 \text{ g.}$$

$$m_1 = 285.7 \text{ g.}$$

$$w_2 = 43.95 \text{ g.}$$

Concentration #2

$$d = .4369^\circ \text{C.}$$

$$w_2 = 87.90 \text{ g.}$$

$$m_1 = 286.0 \text{ g.}$$

These values are within the experimental error prescribed by the experiment and are in good agreement with the actual value of 297.77. This means that the bromopicrin was as pure as could be determined experimentally. The percentage difference is about 4%.

THE DETERMINATION OF THE SURFACE TENSION

So far as could be ascertained the surface tension of bromopicrin has never been determined before. Since this property in conjunction with the density at any particular temperature by means of the Sugden Parachor would give some evidence about the molecular constitution of bromopicrin, this property was investigated. The procedure followed was that described by Findlay<sup>7</sup> using the Du Nouy apparatus.

The Du Nouy apparatus was calibrated in the usual manner and found to be 5.44 dynes/scale unit. The following data resulted:

#1 Temperature ° C.	Scale Reading	#2 Temperature ° C.	Scale Reading
17.3	73.0	17.5	73.1
17.9	73.9	18.0	73.1
18.2	73.5	18.4	73.5
18.6	73.6	18.95	73.6
19.05	73.6	19.1	73.5
19.3	73.4	19.4	73.2
19.6	73.2	19.7	73.6
19.8	73.0	20.0	73.6
20.0	73.0	20.15	73.6
20.1	73.1	20.2	73.6
20.4	73.4	20.5	73.5
20.6	73.4		
20.8	73.8		
21.0	73.1		
21.1	73.8		
21.5	73.6		

Evaluation of these two runs gives a value for the scale reading at 20° C. for the first run of 73.50 and 73.52 for the second. This results in the value of  $49.98 \pm .5$  dynes/cm. for the surface tension of bromopicrin at 20° C.

#### Sugden's Parachor

Sugden's parachor<sup>12</sup> is a refinement of the application of molar volumes to the problem of molecular constitution. The term parachor signifies comparative volume and is defined by the equation

$$P = \frac{m}{D-d} \gamma^{1/4}$$

where  $m$  is the molecular weight,  $D$  is the density of the liquid,  $d$  is the density of the saturated vapor and  $\gamma$  is the surface tension all measured at the same temperature. In this case  $d$  is negligible since the vapor pressure is very low and the density  $d$  of the vapor is very low as compared with the density of the liquid.

Using the observed values for the density and surface tension of bromopicrin at 20° C., the calculation follows:



$$P = \frac{m}{D-d} \gamma^{1/4}$$

$$m = 297.77 \text{ g.}$$

$$P = \frac{297.77}{2.7939} (49.98)^{1/4}$$

$$D_{20^{\circ}} = 2.7939$$

$$P = 283.39$$

$$\gamma = 49.98$$

The parachor, since it is concerned with molecular constitution, is an additive property and may be calculated from empirically deduced atomic and structural constants. The values listed below were taken from Glasstone<sup>13</sup>:

$$\text{NO}_2 = 73.0$$

$$3\text{Br} = 207.0$$

$$\text{C} = 4.8$$

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$$P = 284.8$$

The agreement between the value of the parachor calculated from the experimental values and that from the empirical atomic and structural values is remarkable, there being a percentage of difference of less than .3% between the two. This in addition to the agreement of the molecular refraction values calculated in the same manner, gives very convincing evidence that the molecular construction of bromopicrin is regular and does not find itself in two forms like some nitro-methanes such as, for example, phenylnitromethane.

#### The Molecular Surface Energy

The molecular surface energy, which is a linear function of the temperature, is easily determined for a given temperature when the surface tension is known and is related to the surface tension by the following equation, attributed to Ransey and Sheilds:

$$E = \gamma (Mv)^{2/3}$$

where E is the molecular surface energy, M is the molecular weight,  $\gamma$  is the surface tension and v the molar volume which may be determined from the density.

The molecular surface energy was calculated using the observed values of the surface tension and the density at 20° C.

$$E = \gamma(Mv)^{2/3}$$

$$M = 297.77 \text{ g.}$$

$$E = 49.98 (297.77 \times .3578)^{2/3}$$

$$\gamma = 49.98 \text{ dynes/cm.}$$

$$E = 49.98 \times 22.467$$

$$v = .3578 \text{ cc./g.}$$

$$E = 1122.90 \text{ dyne cm.}$$

This is a fair evaluation, since the molecular surface energy of water at 20° C. is about 550 dyne cm.

#### THE DETERMINATION OF THE INDEX OF REFRACTION

The index of refraction of bromopicrin was determined with an Abbe refractometer according to the method described by Findlay<sup>7</sup>. The refractometer was thermostated at a temperature of 20° C and the light source was monochromatic, sodium (D) light of wavelength 5893 Å. The following values were determined for the index of refraction,  $n$  at this temperature.

$$1.5790 \pm .0004$$

$$1.5788 \pm .0004$$

$$1.5791 \pm .0004$$

$$~~1.5890 \pm .0004~~$$

1.5790

This results in an average value of  $1.5857 \pm .0004$  for the index of refraction of bromopicrin at 20° C. This value agrees favorably with the value of 1.5831 at 13° C. given by the Handbook of Physics and Chemistry<sup>9</sup>.

#### Calculation of the Molecular Refraction

According to the Lorentz and Lorenz formula

$$k = \frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d}$$

$n$  is the index of refraction of the liquid at a given temperature,  $d$  is the density at the same temperature and  $k$  is a constant nearly independent of tempera-



ture known as the specific refraction. The product of the specific refraction and the molecular weight is defined as the molecular refraction. Using the observed values of the index of refraction and the density determined at 20° C.

$$n = 1.5790 \pm .0004$$

$$d = 2.7939 \pm .0005 \text{ g./cc.}$$

the molecular refraction was calculated from the Lorentz and Lorenz formula as follows:

$$Mk = \frac{(1.5790)^2 - 1}{(1.5790)^2 + 2} \times \frac{1}{2.7939} \times 297.77$$

$$Mk = .1163 \times 297.77$$

$$Mk = 34.631$$

The quantity  $Mk$  is an additive property and may be calculated for most organic liquid compounds from empirically deduced atomic and structural refraction constants. The values listed below for the atomic refraction constants of the constituents of bromopicrin using sodium light were taken from a Handbook of Chemistry<sup>14</sup>.

$$C = 2.592$$

$$3Br = 26.781$$

$$NO_2 = 6.720$$

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$$Mk (CBr_3NO_2) = 36.093$$

This value is in excellent agreement with that calculated above from the observed values of the index of refraction and the density. The percentage of difference is about 4%.

It is possible to assume from the two results above, as in the case of the Sugden Parachor, that bromopicrin is a regularly constituted molecule, having but one stable form.

## THE DETERMINATION OF THE VISCOSITY

The viscosity of bromopicrin was determined by means of an Ostwald viscometer according to the method described by Findlay<sup>7</sup>. The bath was thermostated at 20° C. The viscosity was determined relative to water at 20° C. and the following data was obtained:

Time intervals for water at 20° C. in seconds:

94.4  
94.6  
94.4  
94.4  
94.4

Time intervals for bromopicrin at 20° C. in seconds:

175.4  
175.2  
175.2  
175.2  
175.0

The viscosity, relative to water at 20° C., was calculated from Poiseuille's formula:

$$\frac{n_1}{n_2} = \frac{d_1 t_1}{d_2 t_2}$$

where  $n_1$  and  $n_2$  denote the coefficients of viscosity of the two liquids,  $d_1$  and  $d_2$  their densities and  $t_1$  and  $t_2$  their times of flow. If the viscosity of water at 20° C. is assumed to be 1 cp., the relative viscosity of bromopicrin at 20° C. is found to be 5.19 cp. This is also the value of the absolute viscosity of bromopicrin at this temperature, since the absolute viscosity of water at this temperature is approximately 1 cp. The reciprocal of the viscosity, the fluidity, of bromopicrin at 20° C. is 16.92 l/poises.

## SOLUBILITY IN WATER

According to the previous data on bromopicrin obtainable, this liquid is immiscible in water. During the course of this work it was observed that



this is not, strictly speaking, valid. While the bromopicrin was being prepared in the manner previously mentioned, it was noticed that the upper water layer of the distillate was always colored to some degree, the color being similar to that of the bromopicrin. In order to determine whether any bromopicrin was present in this layer the following procedure was followed.

250 cc. of the water layer was shaken violently with an equal volume of absolute ether. The water layer, however, remained discolored even after a long period of violent agitation. The two layers were then left standing in contact. No change was observed until the fifth day, when it was noticed that the lower water layer was completely decolorized. On the other hand the upper layer, too, still remained uncolored. The ether layer was then extracted and the ether solution distilled by reducing the pressure and not applying any heat. When the ether layer had distilled about 3 cc. of impure bromopicrin remained. When purified the yield amounted to approximately 2 cc. of bromopicrin.

This procedure was repeated a number of times and in every case no change was observed in the water layer until the fifth or sixth day. The yield in each case amounted to about 2 cc. of bromopicrin for every 250 cc. of water in the distillate. From this it may be inferred that the bromopicrin is not wholly insoluble in water, but that it dissolves to the extent of 2 cc. per 250 cc. of water, or about 8 cc. per liter of water.

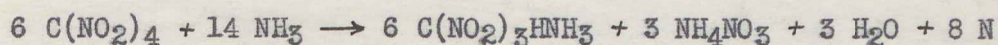
Further evidence was given to this point when 2 cc. of bromopicrin was shaken with 250 cc. of distilled water. The bromopicrin did not dissolve at room temperature, but when the water was heated before hand to about 80° C. the bromopicrin did dissolve and did not separate upon cooling or upon long standing. The water assumed the same color as previously observed. A quantity larger than 2 cc. would not all dissolve, however, at any temperature.



## THE REACTION IN LIQUID AMMONIA

The objective of this particular research was in the beginning to study the reaction of bromopicrin in liquid ammonia, providing such a reaction took place. The reaction of bromopicrin in liquid ammonia was to be one part of a series of investigations to be undertaken in this laboratory under the direction of Dr. F. C. Schmidt. The whole experiment was to consist of a study of the reaction in liquid ammonia of the five compounds in the series beginning with tetranitromethane and ending with tetrabromomethane; that is to say, the study of the reactions of trinitro-bromomethane, dinitro-dibromo-methane and tribromo-nitro-methane (bromopicrin) in liquid ammonia. The reactions of the terminal compounds of this series in liquid ammonia are definitely known. The reaction of tetra-nitro-methane has been studied by Kraus and Franklin<sup>15</sup>. Tetrabromo-methane does not react with liquid ammonia.

The reaction of tetranitromethane in liquid ammonia is a very peculiar and quite unexpected one. This compound first forms an unstable addition product with the ammonia, the formula of which is thought to be  $C(NO_2)_4 \cdot NH_3$ . This compound dissolves in liquid ammonia and the tetranitromethane then reacts, evolving nitrogen, forming ammonium nitrate, water and nitroform ammonia. The equation for this reaction is attributed to Kraus and Franklin<sup>15</sup>, whose experimental work gave conclusive evidence for this equation:



## OBSERVATIONS ON THE REACTION

Obviously the first step in the study of the reaction in liquid ammonia was a qualitative one to determine whether or not such a reaction existed. Approximately two grams of pure bromopicrin were sealed in a glass bulb and submerged in a small Dewar flask filled with liquid ammonia. Upon being immersed



in the liquid ammonia the bromopicrin solidified to a white crystalline mass. The glass bulb was then broken and immediately a violent reaction took place.

An evolution of bubbles, almost explosive in character, occurred, which was probably due to the heat of reaction. The liquid ammonia became a yellow-orange in color, very similar to the color of an aqueous sodium dichromate solution. There appeared to be a primary reaction taking place before the bromopicrin dissolved in the liquid ammonia. At the interface of the solid bromopicrin and the liquid ammonia, a brownish-orange layer was formed which appeared to be a somewhat viscous solid. The formation of an interfacial layer such as this was observed by Kraus and Franklin<sup>15</sup> and was mentioned previously. Its formation here may well be that of an addition compound of the formula  $\text{CBr}_3\text{NO}_2 \cdot n\text{NH}_3$ . This layer dissolved in the liquid ammonia as rapidly as it was formed. Throughout the course of the reaction it appeared that a gas was being evolved as shown by the small bubbles formed. Upon the complete dissolution of the solid bromopicrin, the Dewar flask was left standing in order to allow the liquid ammonia to evaporate.

#### THE REACTION PRODUCT

After the liquid ammonia had vaporized off, a brilliant yellow mass, which appeared to be crystalline and homogeneous, was left behind in the Dewar. This reaction product seemed to be stable, but was found, on the other hand, to be very unstable. This yellow mass was observed to be stable only in the presence of a fairly concentrated atmosphere of ammonia. When this atmosphere was removed the reaction product immediately decomposed in the presence of the air.

Upon decomposing in the presence of the air, this brilliant yellow mass became gray, moisture was formed on the walls of the receptable, and the



odor of hydrogen cyanide was detected. This air-decomposed product was immediately taken up with water, the whole amount did not dissolve, and the solution gave a very conclusive test for acidity. However, after twenty-four hours this same solution was neither basic nor acidic. This would confirm the presence of hydrogen cyanide during the process of decomposition. Furthermore this solution gave a positive test for the bromide ion with silver nitrate.

When the yellow reaction product was dissolved in pure water in the absence of air, the substance again decomposed, but in a totally different manner from the way it decomposed in air. The water solution became a light orange in color and it appeared as though free bromine was evolved by the decomposition, which in turn dissolved in the water. All of the yellow reaction product dissolved in the water. This solution was neither acidic nor basic. Furthermore, this solution gave positive qualitative tests for the bromide ion and also free bromine as well. The addition of 5% HCl solution to this water solution decolorized it and the further addition of 5% NaOH caused the original color to return. Dilute or concentrated sodium hydroxide had no observable effect on the solution. The solution could not be decolorized with ether, benzene or carbon tetrachloride.

When the yellow ammonia reaction product was dissolved in ethanol in the absence of air, no decomposition resulted, although not all the reaction product dissolved. A finely divided white powder was left unsolvated. The solution was a yellow-orange color. After the ethanol had vaporized off, the original brilliant yellow ammonia reaction product was left, which immediately decomposed in contact with the air as described before.

At this point the following probabilities may be advanced. The ammonia reaction product is a mixture of two substances: one, an inorganic salt,



a bromide, probably ammonium bromide, and an organic compound, which has a yellow color. The organic compound is easily oxidized by the oxygen of the air. This conclusion was reached because if it were the moisture of the air which caused it to decompose, then its decomposition in this medium should follow that in water, which it does not.

The test for free bromine in the water-decomposed solution is not necessarily conclusive, since it is possible that the organic compound present might oxidize the potassium iodide to free iodine.

RATIO OF WEIGHT OF BROMOPICRIN TO THE WEIGHT OF  
LIQUID AMMONIA REACTION PRODUCT

In order to study the liquid ammonia reaction more quantitatively, the following apparatus was devised. A carefully weighed, eight inch test tube, fitted with a rubber, one-holed stopper, in which a calcium chloride drying tube was inserted filled with calcium chloride, was suspended in a Dewar flask filled with liquid ammonia. The test tube itself was filled with liquid ammonia and a weighed portion of bromopicrin sealed within in a small glass bulb was then introduced into the test tube. The bulb was then broken and the reaction allowed to proceed. The ammonia in vaporizing formed a compound with the calcium chloride sealing the test tube and preventing the entrance of the air. In this way the reaction product did not decompose after the liquid ammonia had completely vaporized, since an atmosphere of ammonia still remained in the test tube. Upon completion of the reaction the test tube was weighed quickly before the reaction product decomposed.

<u>Weight of CBr<sub>3</sub>NO<sub>2</sub></u> <u>in grams</u>	<u>Weight of Reaction Prod.</u> <u>in grams</u>
2.0015	2.3380
3.1176	3.6478



This results in a ratio of the weight of bromopierin to the weight of the solid reaction product in the first case of 1:1.155 and in the second case of 1:1.156. Since in all probability a gas is developed during this reaction this ratio does not give evidence as to the total weight of the reaction product.

#### DETERMINATION OF BROMINE IN THE LIQUID

##### AMMONIA REACTION PRODUCT

Obviously, because of the extreme instability of the liquid ammonia reaction product, samples of this substance could not be weighed out directly for testing purposes. This hazard was circumvented by dissolving a known weight of the reaction product in a liter of water. Samples of this solution were used for all testing purposes.

A determination of the amount of bromine existing in the reaction product in the form of the bromide ion or as free bromine was made using Mohr's method<sup>16</sup>.

<u>Weight of Reaction Product in grams</u>	<u>Equiv. Wgt. of AgNO<sub>3</sub> in g.</u>	<u>Equiv. Wgt. of Br in g.</u>
.1826	.2258	.1032
.1826	.2243	.1063

This data yields the values of 56.5% and 58.1% for the percentage by weight of the bromine existing in the liquid ammonia reaction product in the form of bromide and free bromine. This data is, however, subject to some possible limitations. The values given above are given for the percentage by weight of the bromide and free bromine existing in a water solution of the reaction product. This, of course, does not concern the bromine existing in the form of organic material. On the other hand, since the reaction product is known to decompose in water, it is possible that more bromine in the form of the bromide or free bromine



is present in the water solution, due to the decomposition of the organic compound upon solution, than would be present in the undecomposed reaction product. This is more likely the actual case.

DETERMINATION OF FREE BROMINE IN THE WATER SOLUTION  
OF THE AMMONIA REACTION PRODUCT

If it can be assumed that the positive test for free bromine in the water solution of the ammonia reaction product is valid and is not due to an oxidation of the potassium iodide to free iodine by the organic compound present in the solution, the amount of bromine present in the form of bromide may be readily determined in this way. The total amount of bromine in the water solution has been found. If, now, the amount of bromine as free bromine can be determined, the difference will yield the desired information. This procedure was undertaken.

An excess of potassium iodide was added to a sample of the water solution containing a known weight of the reaction product, iodine was produced and this was titrated with standard thiosulphate solution using starch as an indicator<sup>17</sup>.

<u>Weight of Reaction</u> <u>Product in grams</u>	<u>Weight of Br</u> <u>in grams</u>	<u>Percent of Br</u> <u>by Weight</u>
.1826	.0265	14.5
.1826	.0266	14.6

This results in a value of approximately 42.8% by weight for the amount of bromine in the form of a bromide in the ammonia reaction product.

In the light of this data, it is impossible to <sup>write</sup> the equation for the reaction which is taking place. All that can be said is that the reaction does

occur, that it appears as if a gas were being evolved, probably nitrogen; that a bromide salt is formed to the amount of 42.8% by weight, probably ammonium bromide and that also an organic compound of unknown structure is formed. In order to ascertain conclusively just what reaction occurs here, the following investigations must be undertaken. The amount of the gas evolved must be measured quantitatively and its identity proven. The inorganic salt must be proven to be ammonium bromide. And in conclusion the organic salt must be separated from the inorganic salt and its structure defined. Time did not permit these investigations taking place.

#### SUMMARY

The density and the index of refraction of bromopicrin were verified. New values were determined for the vapor pressure and the melting point.

The surface tension and the viscosity were measured for the first time.

The Sugden Parachor, heat of vaporization, molecular surface energy, molecular refraction and the fluidity of bromopicrin were calculated from observed values.

The solubility in water was found to be about 23% at higher temperatures.

A preliminary investigation of its reaction in liquid ammonia was successfully made.



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